Thermal Conductivity and Thermal Diffusivity

of the Refrigerant Mixtures R507, R404A, R410A, and R407C[1]

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Abstract

The paper presents a mathematical model for the computation of the thermal conductivity and thermal diffusivity of fluid mixtures in the low density region up to saturation conditions over a wide temperature range approaching the liquid-vapor critical point. Our special interest is focused on systems containing polyatomic molecules whereby the refrigerant mixtures of technical importance R404A, R507, R410A, and R407C are object of our investigations. The model for the calculation of the thermal conductivity is based on the kinetic gas theory, and equations for the transport coefficients are correlated with experimental data. The transport properties at high density are obtained from the region at low-pressure by the use of density-sensitive functions which are empirically correlated. In these correlations we consider the acentric factor, dipole moment, molecular structure, polarity, and the hydrogen bonding effect. To take into consideration the rotational effect, we use a correction factor on the basis of a elastic smooth-sphere model. For data comparison the theoretical results for the thermal conductivity are converted to thermal diffusivity using values for the density and specific heat capacity at constant pressure. For this, a model based on kinetic theory, is applied. The model for the calculation of the equilibrium properties of the refrigerant mixtures studied in this work contains all important molecular contributions, e.g., translation, rotation, internal rotation, vibration, intermolecular potential energy, and the influence of electron and nuclei excitation. The analytical results for the thermal diffusivity are in excellent agreement with the experimental data from dynamic light scattering (DLS).

Keywords: Speed of sound, viscosity, refrigerants

1. INTRODUCTION

In technical practice, fluid mechanics processes are of vital importance. The mathematical theory of chaos may in the future contribute to our understandings of turbulent flow. At this time in practical engineering for the prediction of turbulence is almost in all cases used the classical models such as k-ε or k-ω model. Today are on the market many excellent models (CFX, FIRE, IDEAS,….) for the use in fluid engineering. One of the main problems of presented models is hidden in relatively weak database of thermophysical properties. Almost in all cases are thermophysical properties represented as constants independent on the temperature and pressure field. In this paper we try to present the importance of thermophysical properies for the studying of advanced fluid mechanics.

In order to design devices of this field of activity, it is necessary to be familiar with the equilibrium and nonequilibrium thermodynamic properties of state in a one and two phase environment for pure compounds and their mixtures.

In these paper we developed the mathematical model of computing the transport properties of state. The results of the analysis are compared with experimental data by dynamic light scattering (DLS) [1-3] and show a relatively good agreement.

2. KINETIC THEORY OF POLYATOMIC FLUIDS

From the semi-classical kinetic theory for polyatomic fluids [4-8] we can express the coefficient of thermal conductivity λ, shear viscosity η and bulk viscosity κ_s:

$$\lambda = \frac{2k^2T}{3m}[A,A], \quad \eta = \frac{1}{10}kT[B,B], \quad \kappa_s = kT[\Gamma,\Gamma] \qquad (1)$$

where A, B and Γ are complex vector, tensor and the scalar functions. The detailed description of physical origin of bulk viscosity is explained in the literature [6]. It arises in dense polyatomic gases and liquids.

Available literature [4-11] indicates that in collisions between rotating molecules generally only one or a few quanta of rotational energy are exchanged and since the rotational quantum for fluids at ordinary temperatures is much smaller than the relative kinetic

energy of a colliding pair, the assumption for very small influence of rotational energy is accurate. Furthermore, for the vibrational degrees of freedom, we note that at normal temperatures only the lowest vibrational energy states are occupied. Thease is the reason that in our model is inelastic scattering completely ignored and that the cross section is independent of the internal states of the molecules. In such a case original bracket integral equations are reduced for those in monoatomic gas.

From the Boltzmann equation we can for mono-atomic dilute gases calculate transport properties not far from the Maxwellian [4]. Thease means, that we treat transport phenomena with small temperature or velocity gradients of the molecules. On thease basis we can express thermal conductivity for single-component gas:

$$\lambda_0 = \frac{25kTC_V}{16M\Omega^{(2,2)}} \left(1 + \frac{2}{21} \left(\frac{\Omega^{(2,3)}}{\Omega^{(2,2)}} - \frac{7}{2} \right)^2 \right) \qquad (2)$$

where M is molecular mass of the molecule, C_V is isochoric specific heat and $\Omega^{(l,s)}$ is the transport collision integral. For Leenard-Jones intermolecular potential is almost impossibly obtain collsision integrals analytically. Because of difficulty of calculating these integrals, their values are usually taken from published tables. To make computerized calculations more convenient and to improve on the accuracy obtainable

by linear interpolation of the tables we used Neufeld [8] at al. empirical formulation, obtained on the basis of numerical simulations and interpolation procedure.

$$\Omega^{(l,s)*} = \frac{A}{T^{*B}} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)} + RT^{*B}\sin(ST^{*W} - P) \qquad (3)$$

This Equation contains 12 adjustable parameters and is developed for 16 collision integrals.

For the calculation of transport properties for polyatomic molecules in principle, a quantum mechanical treatment of processes is necessary to account for the changes of internal state. The fully quantum mechanical kinetic theory of polyatomic gases is based on Waldman-Snider [5,6] equation and summarized by McCourt and coworkers. Wang-Chang and Uhlenbeck and independently by de Boer (WCUB) formulated a semiclassical kinetic theory. The quantum mechanical theory has the advantage that it can treat the degeneracy of rotational energy states and is therefore able to describe the effect of magnetic and electric fields on the transport properties. The disadvantage of this theory for practical applications is that it is only formally established for gases with rotational degrees of freedom. On the other hand, the semiclassical theory has the advantages that it treats all forms of internal energy and is the semiclassical limit of the quantum mechanical approach. In the presented paper we used simple expressions for taking into account rotational contributions. Internal modes have, at relatively low temperatures, almost no influence on viscosity and relatively high influence on thermal conductivity.

In the presented paper will be presented Chung-Lee-Starling model [9-11] (CLS). Equations for the viscosity and the thermal conductivity are developed based on kinetic gas theories and correlated with the experimental data. The low-pressure transport

properties are extended to fluids at high densities by introducing empirrically correlated,

density dependent functions. These correlations use acentric factor ω, dimensionless dipole moment μ_r and empirically determined association parameters to characterize molecular structure effect of polyatomic molecules κ, the polar effect and the hydrogen bonding effect. In this paper are determined new constants for fluids.

The dilute gas viscosity for CLS model is written as:

$$\eta_0(T) = 26.69579 \cdot 10^{-1} \frac{\sqrt{MT}}{\Omega^{(2,2)*}\sigma^2} F_c \tag{4}$$

where η is in Pa s, M is the molecular mass in $gmol^{-1}$, T is in K, $\Omega^{(2,2)}$ is a collision integral and σ is the Lennard-Jones parameter.

The factor F_c has been empirically found to be [10]:

$$F_c = 1 - 0.2756\omega + 0.059035\mu_r^4 + \kappa \tag{5}$$

where ω is the acentric factor, μ_r relative dipole moment and κ is a correction factor for hydrogen-bonding effect of associating substances such as alcohols, ethers, acids and water.

For dense fluids Eq. (4) is extended to account for the effects of temperature and pressure by developing an empirically correlated function of density and temperature as shown below:

$$\eta = \eta_k + \eta_p \tag{6}$$

$$\eta_k = \eta_0 \left(\frac{1}{G_2} + A_6 Y \right) \tag{7}$$

$$\eta_p = \left[36.344 \cdot 10^{-6} - (MT_c)^{.5} / V_C^{2/3} \right] A_7 Y^2 G_2 \exp(A_8 + A_9 / T^* + A_{10} / T^{*2}) \tag{8}$$

$$Y = \rho V_c / 6, \quad G_1 = \frac{1.0 - 0.5Y}{(1.0 - Y)^3}, \quad T_c = \frac{1.2593\varepsilon}{k}, \quad V_c = \left(0.809\sigma\left(\mathring{A}\right)\right)^3 \tag{9}$$

$$G_2 = \frac{\{A_1(1 - \exp(-A_4 Y)) + A_2 G_1 \exp(A_5 Y) + A_3 G_1\}}{(A_1 A_4 + A_2 + A_3)} \tag{10}$$

The constants A_1-A_{10} are linear functions of acentric factor, reduced dipole moment and the association factor

$$A_i = a_0(i) + a_1(i)\omega + a_2(i)\mu_r^4 + a_3(i)\kappa, \ i=1,10 \tag{11}$$

where the coefficients a_0, a_1, a_2 and a_3 are presented in the work of Chung at al. The same approach was employed to develop expression for thermal conductivity:

$$\lambda = \lambda_k + \lambda_p \tag{12}$$

where:

$$\lambda_k = \lambda_0 \left(\frac{1}{H_2} + B_6 Y\right) \tag{13}$$

The thermal conductivity in the region of dilute gases for CLS model is written as:

$$\lambda_0 = 3119.41 \left(\frac{\eta_0}{M}\right)\psi \tag{14}$$

where ψ represents the influence of polyatomic energy contributions to the thermal conductivity. We used the Taxman theory [5]. He solved the problem of influence of internal degrees of freedom on the basis of WCUB theory [6] and the approximations given by Mason and Monschick [6,7,12]. The presented expression is more accurate than Eucken correction [6] and the equation is supported with theory. The final expression for the influence of internal degrees of freedom is represented as:

$$\psi = 1 + C_{int}^{*} \left\{ \dfrac{0.2665 + \dfrac{(0.215 - 1.061\beta)}{Z_{coll}} + 0.28288 \dfrac{C_{int}^{*}}{Z_{coll}}}{\beta + \dfrac{0.6366}{Z_{coll}} + \dfrac{1.061\beta C_{int}^{*}}{Z_{coll}}} \right\} \tag{15}$$

where C_{int}^{*} is the reduced internal heat capacity at constant volume, β is diffusion term and Z_{coll} is the collision number, and is defined as the number of collisions required to interchange a quantum of internal energy with translational energy. In the presented paper is used the correlation of Z_{coll} developed by Chung, Leee and Starling [10]:

$$Z_{coll} = 2.0 + 10.5 \dfrac{T}{T_c} \tag{16}$$

The heat capacities of ideal gases are calculated by use of statistical thermodynamics. The paper features all important contributions (translation, rotation, internal rotation, vibration, intermolecular potential energy and influence of electron and nuclei excitation). The transport term β is possibly to obtain analytically as the ratio between viscosity and the product between self-diffusivity at dilute gas conditions and density and shear viscosity. In our case we have used the correlation function obtained on the basis of Pitzer acentric factor ω [9]:

$$\beta = 0.786231 - 0.710907\omega + 1.31583\omega^{2} \tag{17}$$

The residual part λ_p to the thermal conductivity can be represented with the following equation

$$\lambda_p = \left(0.1272 \left(\dfrac{T_c}{M} \right)^{1/2} \dfrac{1}{V_c^{2/3}} \right) B_7 Y^2 H_2 \left(\dfrac{T}{T_c} \right)^{1/2} \tag{18}$$

where λ_p is in W/mK.

$$H_2 = \left\{ \begin{array}{l} B_1[1-\exp(-B_4Y)]\dfrac{1}{Y} + \\ B_2G_1\exp(B_5Y) + B_3G_1 \end{array} \right\} \dfrac{1}{B_1B_4 + B_2 + B_3} \tag{19}$$

The constants B_1-B_7 are linear functions of acentric factor, reduced dipole moment and the association factor

$$B_i = b_0(i) + b_1(i)\omega + b_2(i)\mu_r^4 + b_3(i)\kappa, \quad i=1,10 \tag{20}$$

where the coefficients b_0, b_1, b_2 and b_3 are presented in the work of Chung et al.[14,15]

3. THE PREDICTION OF THERMAL CONDUCTIVITY OF MIXTURES

For the determination of thermal conductivity for fluid mixtures we have used purely analytical model [5]. According to this theory the thermal conductivity of dense gas mixtures containing N components can be written in the form:

$$\lambda = -\frac{\begin{vmatrix} \Lambda_{11} & \cdots & \Lambda_{1N} & \psi_1 \\ \vdots & & \vdots & \vdots \\ \Lambda_{N1} & & \Lambda_{NN} & \psi_N \\ \psi_1 & & \psi_N & 0 \end{vmatrix}}{\begin{vmatrix} \Lambda_{11} & \cdots & \Lambda_{1N} \\ \vdots & & \vdots \\ \Lambda_{N1} & \cdots & \Lambda_{NN} \end{vmatrix}} \tag{21}$$

For N=1 the expression (21) reduces to the one-copmonent gas equation.

$$\Lambda_{ii} = \frac{\psi_i^2}{\lambda_i} + \sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{\psi_i\psi_j}{2\lambda_{ij}A_{ij}^*} \frac{M_iM_j}{(M_i+M_j)^2} \left(\frac{\frac{15}{2}M_i^2 + \frac{25}{4}M_j^2 - 3M_j^2B_{ij}^* + 4M_iM_jA_{ij}^*}{(M_i+M_j)^2} \right) \tag{22}$$

$$\Lambda_{ij}(j\neq i) = -\frac{\psi_i\psi_j}{2\lambda_{ij}A_{ij}^*}\frac{M_iM_j}{(M_i+M_j)^2}\left(\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^* \right) \tag{23}$$

where ρ is the molar density, ψ_i and ψ_j are mole fractions of species i and j, and M_i and M_j are their molecular masses. A_{ij}^* and B_{ij}^* are a weak function of intermolecular potential for i-j interactions. Both coefficients we have calculated with help of Neufeld et al. expression for reduced collision integrals[5].

$$A_{ij}^* = \frac{\Omega_{ij}^{(2,2)*}}{\Omega_{ij}^{(1,1)*}}, \qquad B_{ij}^* = \frac{\left(5\Omega_{ij}^{(1,2)*} - 4\Omega_{ij}^{(1,3)*}\right)}{\Omega_{ij}^{(1,1)*}} \qquad (24)$$

The symbol λ_i represents the viscosity of pure component i and λ_{ij} represents the thermal conductivity of i-j interaction:

$$\lambda_{ij} = \sqrt{\lambda_i \lambda_j} \qquad (25)$$

4. THERMAL DIFFUSIVITY

In heat transfer analysis, the ratio of the thermal conductivity to the heat capacity is an important property termed the thermal diffusivity α. Materials with large thermal diffusivity will respond quickly to changes in their thermal environment.

$$\alpha = \frac{\lambda}{\rho c_p} \qquad (26)$$

The thermal diffusivity represents the ability of a material to conduct thermal energy relative to its ability to sore thermal energy. In our case we have used the Tillner et al. model for calculation of isobaric specific heats [13].

5. RESULTS AND COMPARISON WITH EXPERIMENTAL DATA

Figures 1-8 show the deviation of the results for thermal conductivity and thermal diffusivity for refrigerant mixtures R507, R407C, R410A and R404A in the saturated gas region and saturated liquid region between the analytical computation (CLS-Chung-

Lee-Starling model), REFRPROP 7.0 model (REF), Sovay package 3.1.3 (S) and DLS experimental technique. The detailed description of DLS experimental technique is explained in the literature [1-3]. The relative deviation (RD) is defined between CLS and REF model by the next expression:

$$RD(CLS-REF) = \frac{(data_{CLS} - data_{REF})}{data_{REF}} \qquad (27)$$

With the same procedure are defined the RD between othe models. From Figures 1,3,5 and 7 is possibly to analyze that the comparison between S and REF model show relatively big deviation with maximum RD more than 25%. Our CLS model yields much better results for thermal conductivity in comparison with S model than in comparison with REF model. The proposed finding is particularly obvious for the saturated vapour range. The results of thermal diffusivity (Fig. 2,4,6 and 8) obtained by the S model shows better agreement witg DLS experimental technique than REF model too.Our CLS model gives relatively accurate results for thermal diffusivity too. Somewhat larger deviations can however be found in the near-critical region due to the large influence of the fluctuation effects [14,15].

6. CONCLUSION AND SUMMARY

The paper presents the mathematical model for computation of transport properties in the liquid, and gaseus state.

The analytical results are compared with the dynamic light scattering technique and show relatively good agreement

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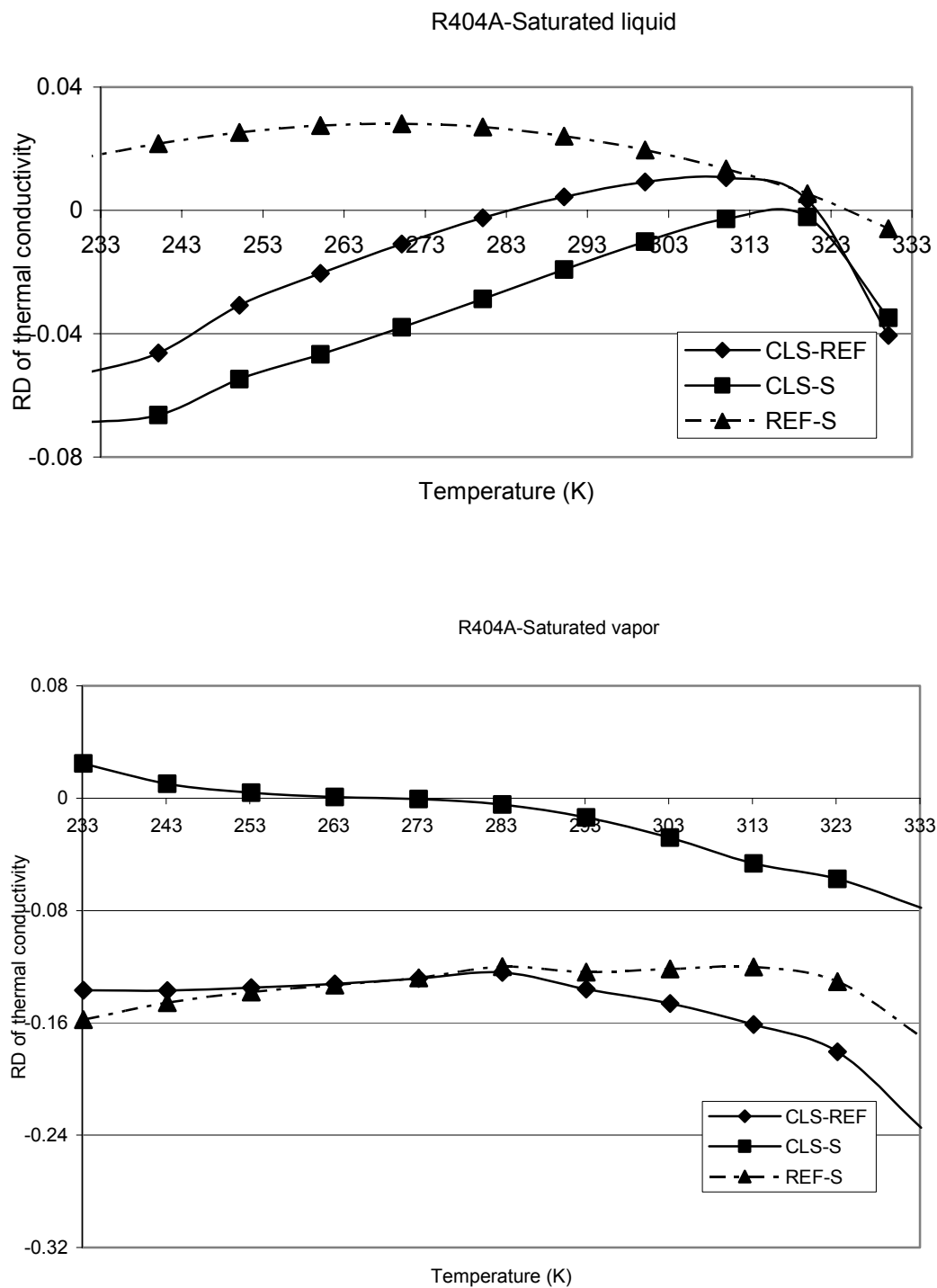
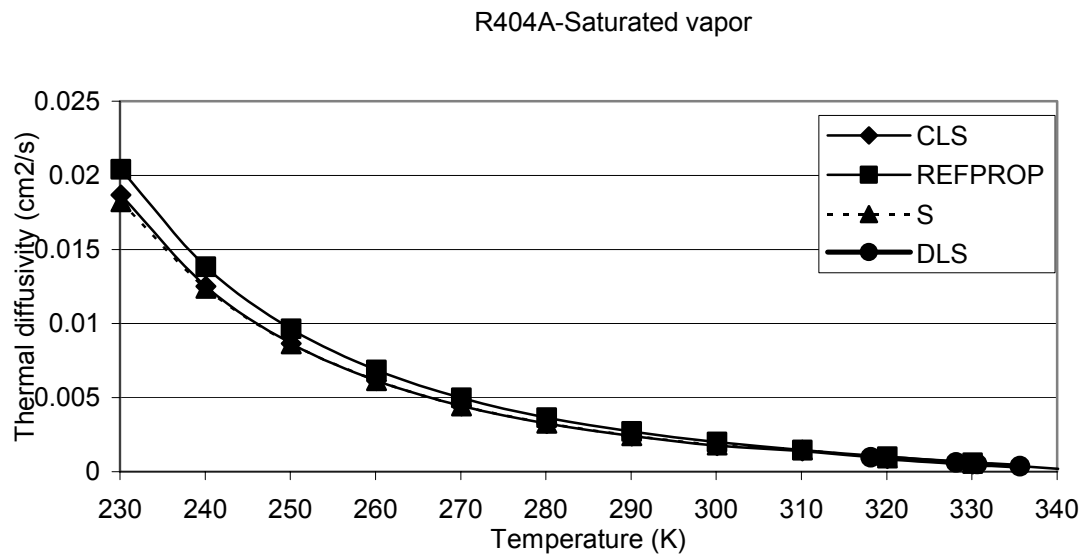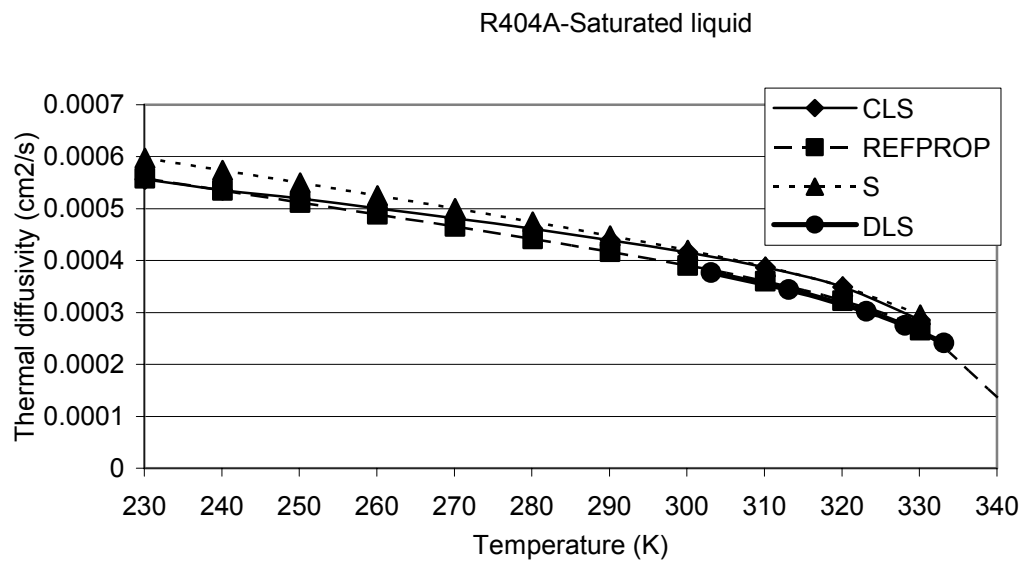**Figure Captions:**

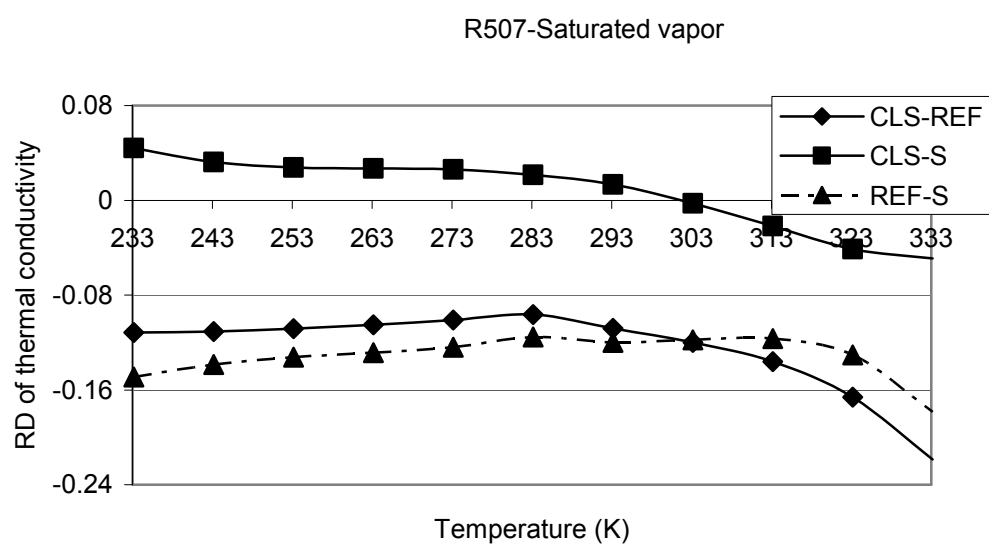Figure 1: Thermal conductivity of R404A
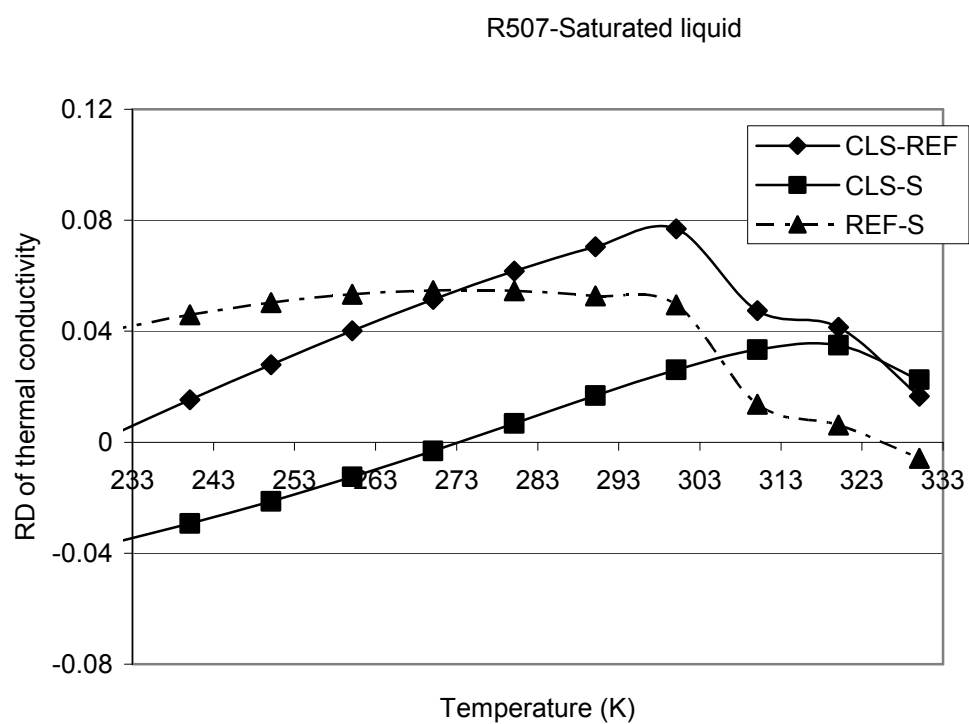
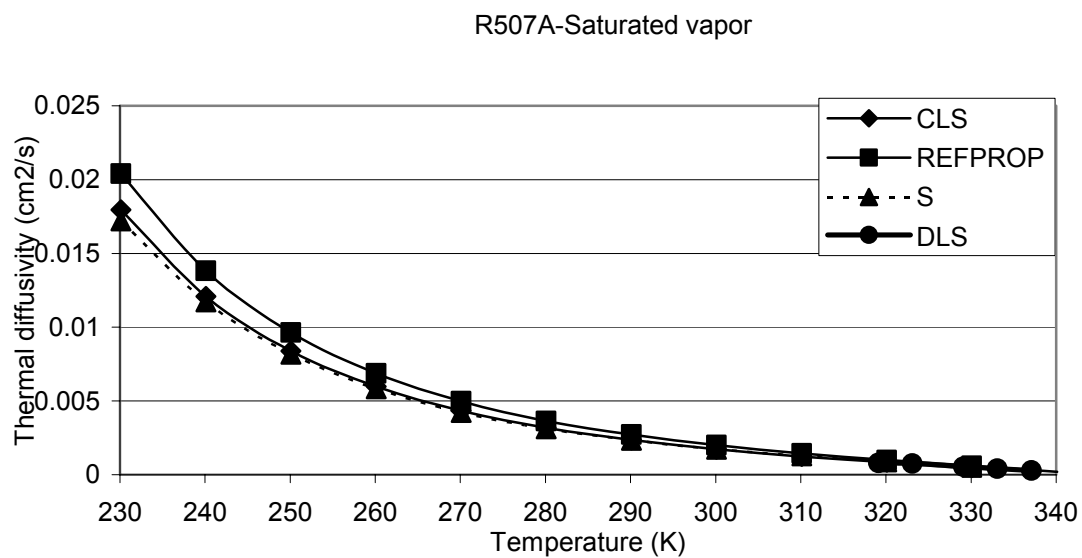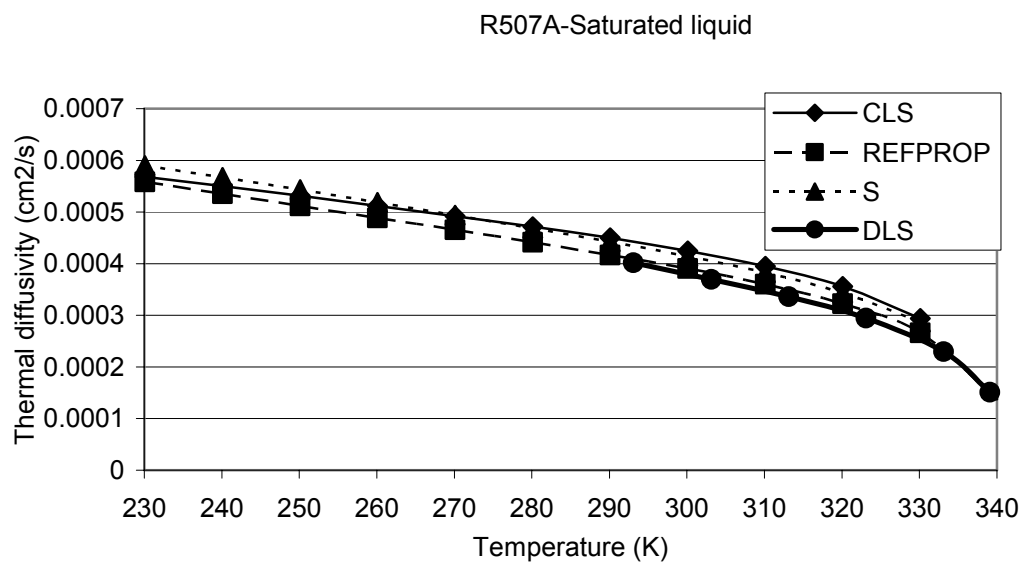Figure 2: Thermal diffusivity of R404A

Figure 3: Thermal conductivity of R507

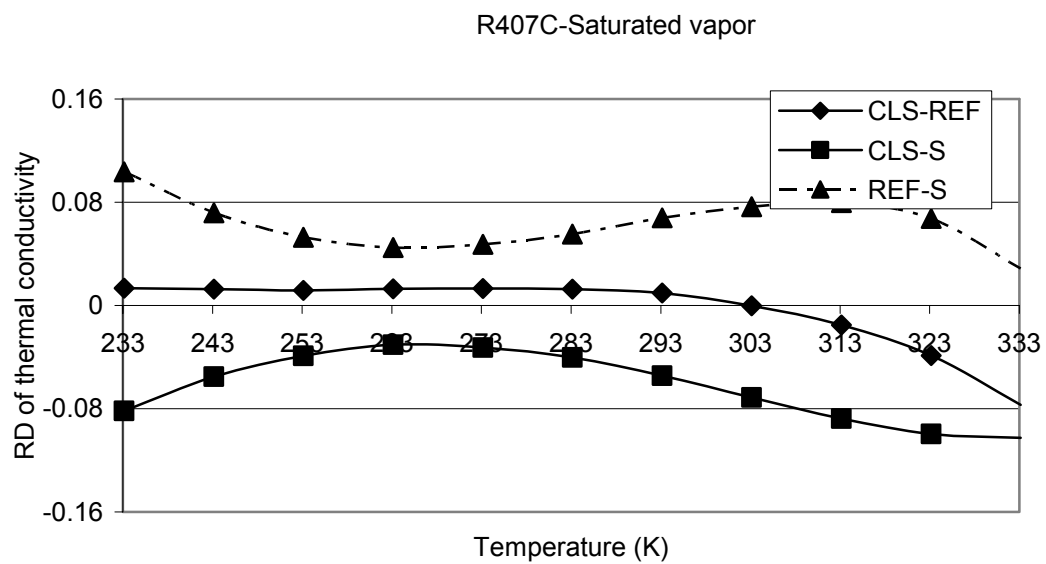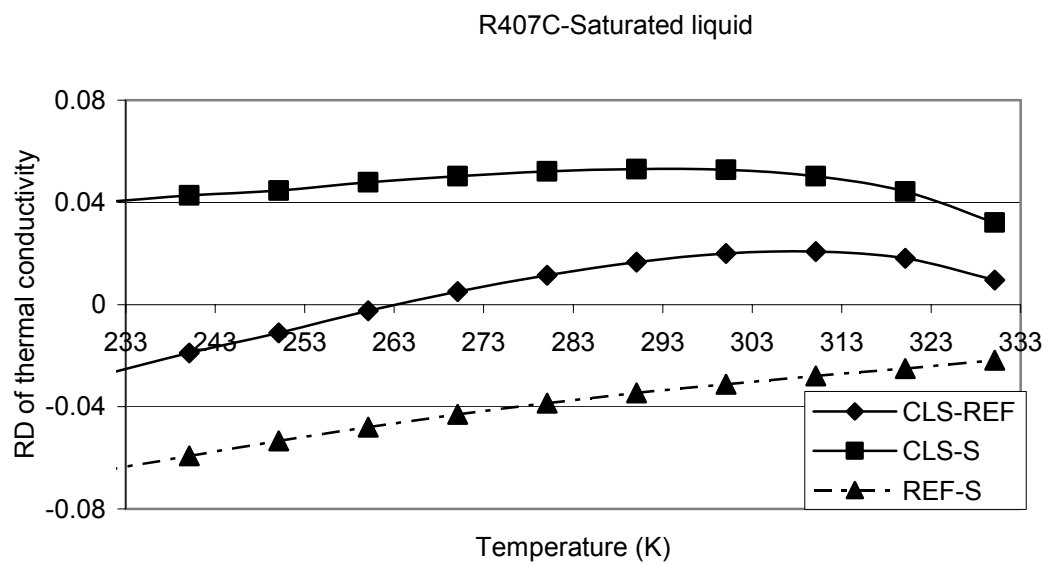Figure 4: Thermal diffusivity of R507

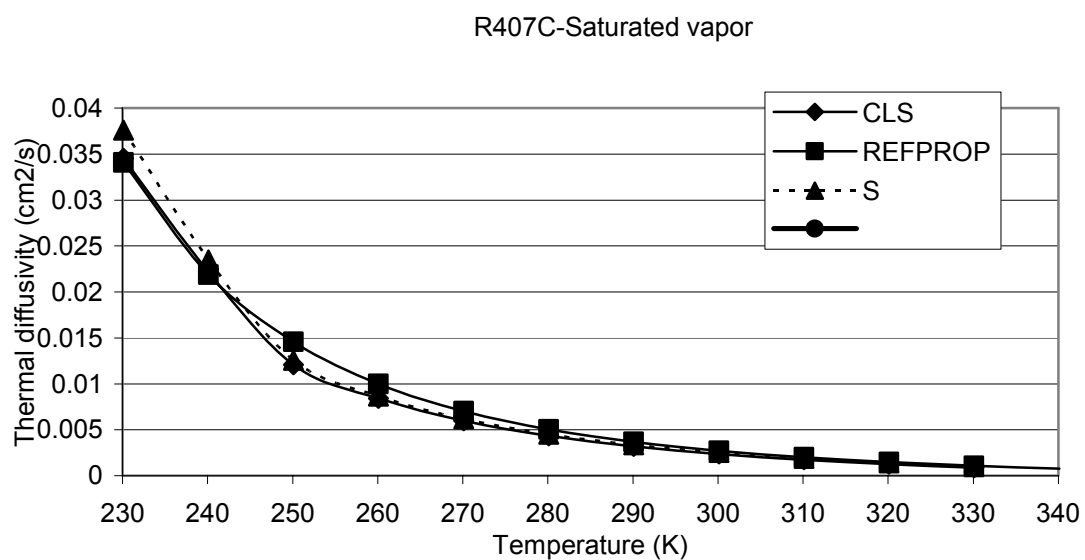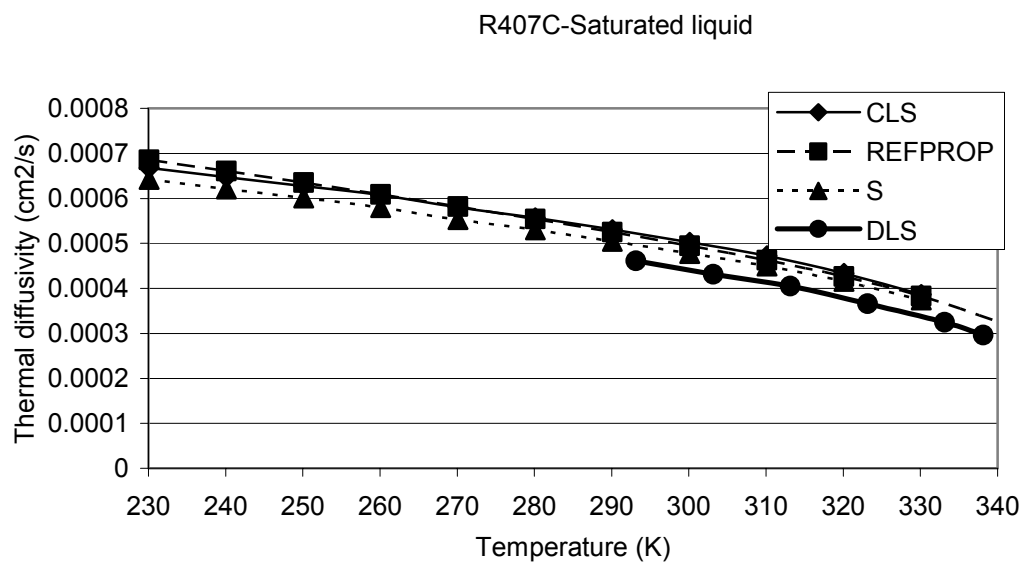Figure 5: Thermal conductivity of R407C
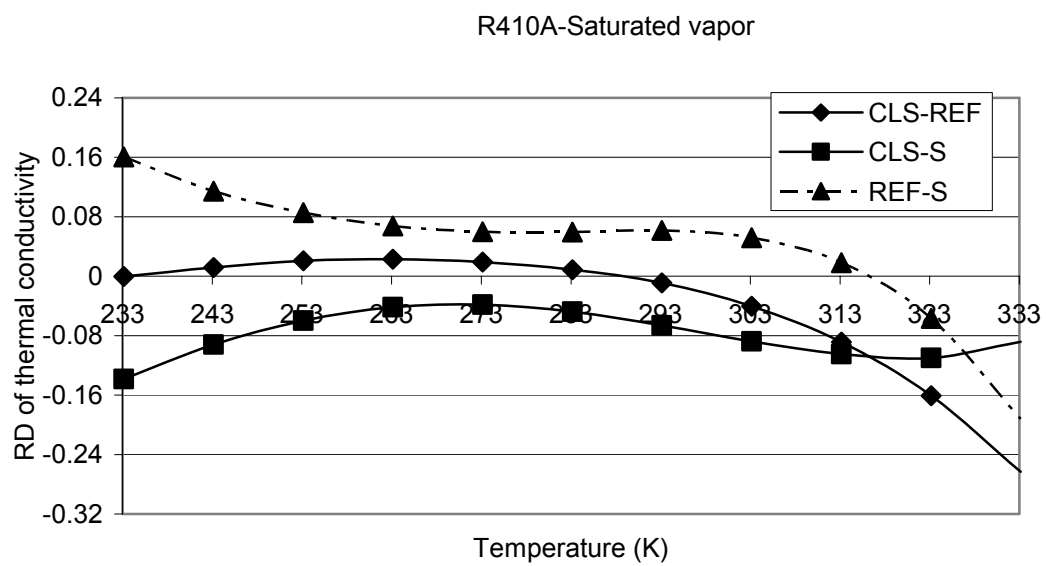
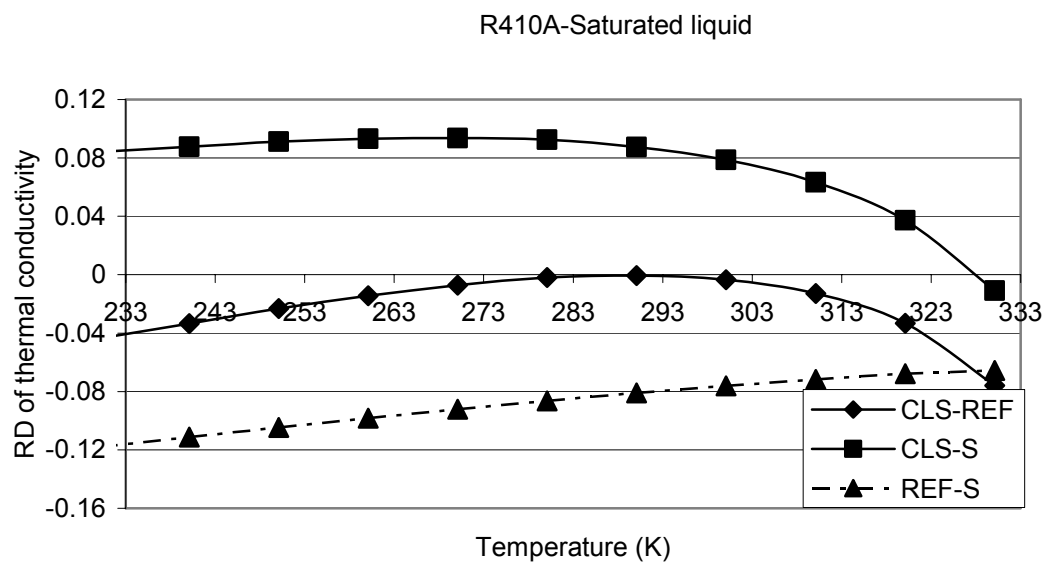Figure 6: Thermal diffusivity of R407C

Figure 7: Thermal conductivity of R410A

Figure 8: Thermal diffusivity of R410A

FIGURES

R404A-Saturated liquid

R404A-Saturated vapor

Figure 1: Thermal conductivity of R404A

R404A-Saturated liquid

R404A-Saturated vapor

Figure 2: Thermal diffusivity of R404A

R507-Saturated liquid

R507-Saturated vapor

Figure 3: Thermal conductivity of R507A

R507A-Saturated liquid

R507A-Saturated vapor

Figure 4: Thermal diffusivity of R507A

Figure 5: Thermal conductivity of R407C

R407C-Saturated liquid

R407C-Saturated vapor

Figure 6: Thermal diffusivity of R407C

R410A-Saturated liquid

R410A-Saturated vapor

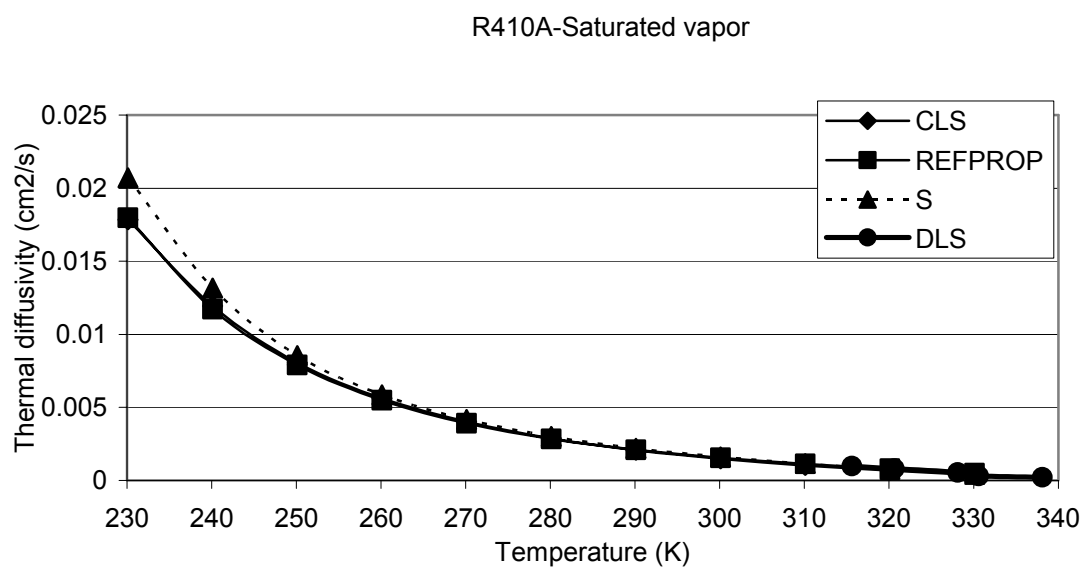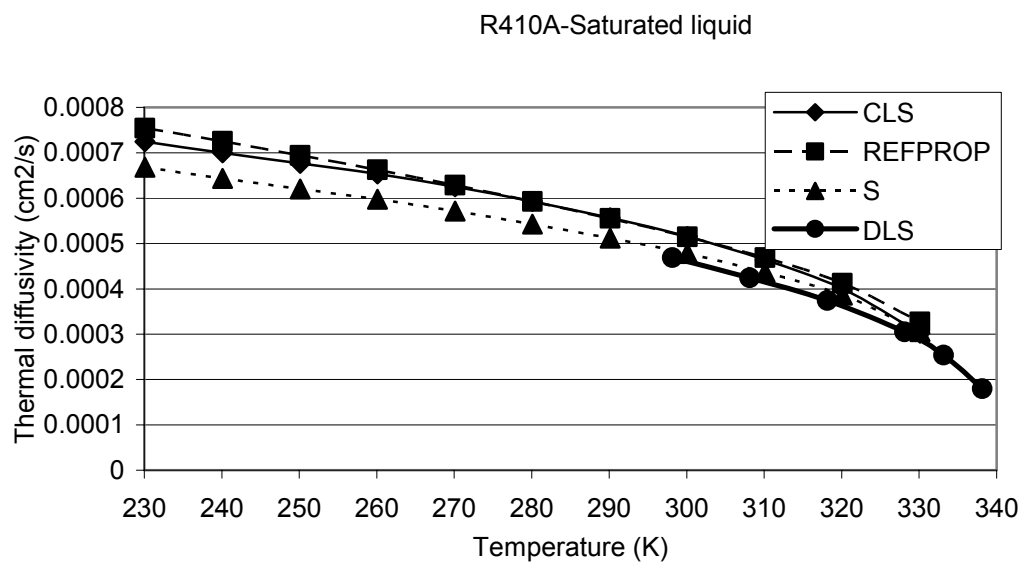Figure 7: Thermal conductivity of R410A

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R410A-Saturated liquid

R410A-Saturated vapor

Figure 8: Thermal diffusivity of R410A